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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

Dec 17 1986

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

## MEMORANDUM

SUBJECT: PP #6F3429/6H5506 (RCB #'s 1600, 1601, 1602, 1603, and 1604) Chlorpyrifos-Methyl (Reldan) in/on Stored Corn. Amendment of 10/21/86. Accession No. 266025

FROM: Cynthia Deyrup, Ph.D., Chemist  
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Hazard Evaluation Division (TS-769)

Cynthia Deyrup

THRU: Charles L. Trichilo, Ph.D., Chief  
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Hazard Evaluation Division (TS-769)

TO: L. Schnaubelt, Product Manager No. 12  
Registration Division

and

Toxicology Branch  
Hazard Evaluation Division (TS-769)

Background

Dow Chemical Company proposed the establishment of permanent tolerances for residues of chlorpyrifos-methyl [0,0-dimethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate] and its metabolite 3,5,6-trichloro-2-pyridinol in/on corn grain at 6.0 ppm. Dow also proposed the establishment of food/feed additive tolerances on corn soapstock at 40.0 ppm, and on corn milling fractions (except flour) at 30 ppm. The original proposal was rejected for the deficiencies cited in RCB's memo of 8/12/86 (PP #6F3429, memo of C. Deyrup). An addendum to that review (dated 8/27/86) cited the potential for the accumulation of residues from the practice of stairstepping, i.e., multiple pesticide treatments of the corn resulting from a single treatment by each owner of the corn as it passes through commerce.

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The amendment of 9/9/86 partially addressed the deficiencies cited in RCB's 8/12/86 review (memo of C. Deyrup, memo of 10/16/86).

#### Present Consideration

The present consideration consists of a cover letter from J.C. Rockwell, Gustafson, to D. Edwards, RD, revised labels, chromatograms, and a copy of the report on residue levels of chlorpyrifos-methyl and 3,5,6-trichloro-2-pyridinol in corn process fractions.

The remaining deficiencies from RCB's previous reviews will be cited below, followed by the petitioner's responses, and RCB's comments/conclusions.

#### RCB's Comments/Conclusions, Memo of 10/16/86, re: Petitioner's Response to Deficiency 4b

Chromatograms of fortified samples were not submitted. Instead, the petitioner has submitted chromatograms of standards. At least a few chromatograms of fortified samples will need to be submitted so that RCB can better evaluate the analytical methodology performance.

The petitioner did not submit any chromatograms reflecting the analysis for residues of chlorpyrifos-methyl in samples of treated, untreated, and fortified deodorized corn oil. Since bleached, refined, deodorized oil is the commodity which is consumed, the petitioner will need to submit these chromatograms. These chromatograms should be run long enough so that other possible residues of concern could be detected.

The petitioner did not submit raw data sheets reflecting the analyses of processed commodities. Tables 1 and 2 (Tab D.1.0.0) summarized the results of the processing studies. For a permanent tolerance, RCB requires the raw data sheets reflecting the analyses. An analytical data sheet submitted with PP #0F2423 contained no information on analyses of bleached, refined, deodorized oil. Therefore RCB will also need the data sheets from the processing studies submitted with PP #6F3429, which does contain information on deodorized oil.

Deficiency 4b is still unresolved.

#### Petitioner's Response, re: Deficiency 4b

The petitioner has submitted chromatograms reflecting the analysis for chlorpyrifos-methyl in fortified samples of corn grain, steepwater, grits, starch, gluten, and soapstock. Chromatograms reflecting the analysis for 3,5,6-trichloro-2-pyridinol in fortified samples of corn meal, grits, gluten/starch, hulls, flour, steepwater, soapstock, and deodorized corn oil

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were also submitted. The petitioner also submitted chromatograms reflecting the analysis for residues of chlorpyrifos-methyl in treated and untreated samples of deodorized corn oil.

The petitioner submitted a copy of a report entitled, "Residues of Chlorpyrifos-methyl and 3,5,6-Trichloro-2-pyridinol in Corn Process Fractions Obtained from Corn Grain Treated with Reldan 4E Insecticide." This report had not been previously available for RCB's review. The report contained the data sheets giving the sample numbers, substrate, and gross and corrected levels of chlorpyrifos-methyl and the pyridinol in treated and untreated samples from the wet and dry milling fractionation studies.

#### RCB's Comments/Conclusions

From the submitted chromatograms of treated, untreated, and check samples from the wet and dry milling fractionation studies and from the data sheets included in the report, RCB concludes that the residue data are adequate. Deficiency 4b is resolved.

#### RCB's Comments/Conclusions, Memo of 10/16/86, re: Petitioner's Response to Deficiency 4d

"...RCB tentatively concludes that the petitioner has demonstrated that residues after deodorizing would be expected to be lower than the residue levels in the original raw agricultural commodity and has adequately characterized the nature of the residue in deodorized oil.

However, Deficiency 4d is still unresolved; for the sake of completeness, RCB needs chromatograms reflecting the analysis for residues of chlorpyrifos-methyl in samples of oil before and after deodorization. After reviewing these chromatograms, RCB will conclude whether or not a food additive tolerance is needed for refined corn oil."

#### Petitioner's Response, re: Deficiency 4d

The petitioner has submitted chromatograms of fortified, check, and treated samples of deodorized corn oil. The petitioner had previously submitted chromatograms of treated and untreated "corn oil." The petitioner explains in the present submission that the commodity was actually refined corn oil, before deodorization.

#### RCB's Comments/Conclusions

RCB concludes that the residue data on "refined deodorized corn oil" are valid; expected residue levels in this commodity will be lower than levels in corn grain treated according to the proposed use. A food additive tolerance is not required. Deficiency 4d is resolved.

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## Other Considerations

### Corn Dust

RCB has recently learned that corn dust is collected at port terminals and is sold to be added to feed. According to Max Spencer, Continental Grain [(212) 207-5277], corn grain dust contains 8-12% protein, is an inexpensive feed additive, and is used by feed companies all over the country. He said that one of their elevators in New Orleans would generate about 15,000 tons of grain dust each year. The dust is pneumatically removed and deposited in bins. The dust from a New Orleans elevator would be typically composed of 60% corn dust, 30-35% soybean dust, with the rest being wheat dust. At a port elevator, the yield of dust is generally about 0.2% of the weight of the corn itself. Mr. Spencer said that Continental runs spot checks of its grain and dust and has found that pesticide residues do tend to concentrate in the dust. Since the commodity is produced by the kernels rubbing against each other during transit or handling, the resulting dust from the kernel surfaces could exhibit higher residue levels than the kernels themselves. Mr. Spencer also said that the aspiration process itself seems to be partly responsible for the concentration of residues in dust.

RCB has no residue data on corn dust and therefore can reach no conclusions on whether data from hulls are translatable to corn dust. The petitioner will need to propose a feed additive tolerance on corn dust; the tolerance should be supported by appropriate residue data. Mr. Spencer said that he would be willing to discuss appropriate protocols with the petitioner.

### Multiple Treatments

In order to avoid residue levels which are over tolerance and which arise from multiple treatments of the corn with Reldan by subsequent owners of the corn, the petitioner proposes that the following statement be added to the Reldan label:

"Prior to treating grain of an unknown history of grain protectant use, or retreating grain which has been previously treated with Reldan 4E, residual levels of the active ingredient chlorpyrifos-methyl should be established using the appropriate analytical method. Copies of this analytical methodology for chlorpyrifos-methyl are available from Residue Group Manager, Agricultural Products Department, Dow Chemical U.S.A., P.O. Box 1706, Midland Michigan, 48640. When retreating grain, adjust rate of application so as to not exceed 6 ppm chlorpyrifos-methyl."

In a cover letter to D. Edwards (RD), the petitioner suggests that Enzy-Tec pesticide detection tabs may be used by grain

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handlers as a preliminary screening method. If an organo-phosphorus based pesticide is present at levels of greater than 1 ppm, enforcement methodology would then be required to determine the identity of the pesticide and the levels present. The petitioner suggests that labels for all grain protectants (i.e., malathion, Actellic, and Reldan) carry the above statement.

#### RCB's Comments/Conclusions

The submitted label requires enforcement methodology to be used whenever the pesticidal history of the corn is unknown. RCB has contacted the following people on the feasibility of requiring the use of chemical analyses before treating corn which is to be stored:

J. Pitchford	Federal Grain Inspection Service
F. Lantermann	Agricultural Stabilization and Conservation Service
D.E. Kuhlman	Professor of Entomology, University of Illinois
J. Schlueter	Pacific Northwest Grain and Feed Association
P.J. Hamman	Professor of Entomology, Texas A & M
L. Hellman	Professor of Entomology, U of Maryland
H. Womack	Professor of Entomology, U of Georgia

A protectant such as Reldan would be applied to the moving stream of corn as it is being augered into the storage bin. Before loading the corn into the bin, the grain elevator operator would have to decide whether or not to treat the corn. If analyses were required before making the decision to treat the corn, the operator may have to wait 3 days for the result of the analysis (one day to mail the sample to the laboratory, one day for the analysis, and one day to receive the results). All of RCB's contacts concluded that this proposal is impractical and would not work.

Professor Kuhlman (U of Illinois) said that there were probably 1000 country elevators in IL alone; IL produces about 1.4 billion bushels of corn per year, and the number of samples to be tested could be prohibitive. Since most of the samples would have to be analyzed during the harvest season, he wondered whether adequate laboratory capacity existed.

Mr. Schlueter (Pacific Northwest Grain and Feed Association) said that private laboratories would charge \$75-95 per analysis and thought that the added cost would be unacceptable. Port terminals, which ship grain to HI and PR in addition to foreign ports, handle millions of bushels of grain each year. He estimated that running one analysis every 10,000 bushels would cost him \$2,250,000 per year in lab fees.

Mr. Pitchford, of the Federal Grain Inspection Service, said that the delay in getting the results of the lab analyses concerned him; even a delay of 3 days could snarl the grain delivery system. During harvest, corn is brought in every day. Rather than

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analyzing each load of grain with an unknown history, RCB suggested sampling and compositing the day's samples and analyzing the day's composite sample. Even though the number of samples to be analyzed would be decreased, Mr. Pitchford said that each day's corn would have to be put somewhere while the operator waited for the analysis results. Generally the grain is put into a rather small dump area where it is held for a few minutes before being augered into the bin. Mr. Pitchford said that the dump areas are too small to accommodate a day's intake of corn. The grain elevator operator would need 3 extra bins to store each day's intake of corn while he waited 3 days for the lab results. Mr. Pitchford said that the situation is actually worse because many grain elevators deal in graded corn. There are 3 major grades of corn which may in turn be subdivided according to moisture content. The different types of corn are stored separately; therefore the problem of storing up to 6 grades of corn while waiting for analytical results and while more corn is being received becomes enormously complex. According to Professors Hamman (Texas A & M) and Womack (U of Georgia), if the corn is kept in the boxcars or trucks until the analytical results are available, demurrage charges would be prohibitively high. Therefore RCB concludes that the label restriction proposed by the petitioner would probably be ignored.

RCB also learned from Mr. Pitchford that elevator operators can't predict how long the corn would be stored; the corn will be sold when the price is right.

RCB's contacts agreed that if a cheap, reliable, fast test for organophosphorus (OP) pesticides existed, testing before binning could be feasible. In a letter to RD, the petitioner suggests that Enzy-tec pesticide detection tabs be used to screen grain with an unknown history; if the tab indicates that OP's are present at a level of more than 1 ppm, then an analysis would be required before treatment. This approach could be practical only if it turns out that very few analyses would need to be made, for the reasons given above. Since the sensitivity of the tabs could vary depending upon the pesticide, the petitioner would need to validate the sensitivity of any screening test toward chlorpyrifos-methyl. The petitioner would also have to show that this approach is practical. Grain elevator operators should be contacted to determine whether they would be willing to use a screening test, and the validity of the screening tests should be checked with appropriate methodology (i.e., the levels of cholineesterase inhibiting residues should be determined if the screen relies upon enzymatic inhibition). The petitioner should cooperate with grain operators so that it can be determined what proportion of the corn would have to be analyzed and whether the results obtained by the operators use of the screen agree with results obtained in the analytical laboratory. Obviously, if 50% or more of the samples would need to be analyzed, the screen would not practical.

Alternatively, if a fast test exists which could determine

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varying levels of OP's, the petitioner could propose a label restriction against treating corn which contains, for example, more than 3 ppm OP, subject to the validation of the sensitivity of such a test toward chlorpyrifos-methyl.

After consulting grain elevator operators, etc., and if such an approach is practical, the petitioner may want to consider the prevention of overtreatment of corn by the use of restrictions on the sites of applications or by instructions relating treatment to pest pressure, etc.

Codex has established a tolerance of 10 ppm chlorpyrifos-methyl on maize. If the proposed tolerance on corn grain is established, there will be a compatibility problem. The present enforcement method determines the pyridinol after hydrolysis of chlorpyrifos-methyl residues; i.e., the method determines parent and pyridinol simultaneously. Therefore, RCB does not believe that it is possible to reconcile the Codex definition (parent) with the US tolerance expression. Neither Canada nor Mexico has established a tolerance for residues of chlorpyrifos-methyl on corn.

#### Recommendations

1. RCB recommends against establishing the proposed tolerance of 6 ppm chlorpyrifos-methyl/metabolite on stored grain. The petitioner needs to submit a revised Section F proposing a tolerance on corn grain dust; this tolerance should be supported by appropriate residue data.
2. RCB concludes that the proposed label requiring enforcement methodology if the corn to be stored is of unknown history seems to be impractical; RCB recommends that the petitioner reevaluate this proposal.
3. RCB recommends that the petitioner interface with grain elevator operators, etc., and then propose the best solution to the problem of multiple treatments to corn, demonstrate the practicality of the proposal, and supply validation data if necessary.
4. RCB suggests that the Product Manager provide the petitioner with an unabridged copy of this review. The petitioner needs to read in detail RCB's Comments/Conclusions given above.

Attachment-International Residue Limit Status

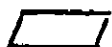
cc:R.F., S.F., Circu, Reviewer, TOX, EEB, EAB, PP#6F3429, FDA, PMSD/ISB

RDI:JHOnley:12/17/86:RDSchmitt:12/17/86

TS-769:RCB:CM#2:RM810:X7484:CDeyrup:cd:12/17/86

INTERNATIONAL RESIDUE LIMIT STATUSCHEMICAL chlorpyrifos - methylPETITION NO 3429CCPR NO. 90

C. Dayrup

F. L. Lee  
7/29/86Codex StatusProposed U. S. TolerancesNo Codex Proposal  
Step 6 or aboveconfirmed  
F. L. Lee 10/15/86

Residue (if Step 9): \_\_\_\_\_

chlorpyrifos - methyl onlyResidue: chlorpyrifos - methyl  
3, 5, 6 - tri chloropyridinolCrop(s) Limit (mg/kg)maize . 10Crop(s) Tol. (ppm)

Corn	6
Corn milling fractions (ex. hulls)	8
Corn Soapstock	40
Meat by-products of cattle, goats, hogs, horses, sheep	1.0
Corn, hulls	30

CANADIAN LIMIT

Residue: \_\_\_\_\_

MEXICAN TOLERANCIA

Residue: \_\_\_\_\_

Crop Limit (ppm)

none

Crop Tolerancia (ppm)

none

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